

Effect of chemical disorder on NiMnSb investigated by Appearance Potential Spectroscopy: a theoretical study

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Abstract. The half-Heusler alloy NiMnSb is one of the local-moment ferromagnets with unique properties for future applications. Band structure calculations predict exclusively majority bands at the Fermi level, thus indicating 100% spin polarization there. As one thinks about applications and the design of functional materials, the influence of chemical disorder in these materials must be considered. The magnetization, spin polarization, and electronic structure are expected to be sensitive to structural and stoichiometric changes. In this contribution, we report on an investigation of the spin-dependent electronic structure of NiMnSb. We studied the influence of chemical disorder on the unoccupied electronic density of states by use of the ab-initio Coherent Potential Approximation method. The theoretical analysis is discussed along with corresponding spin-resolved Appearance Potential Spectroscopy measurements. Our theoretical approach describes the spectra as the fully-relativistic self-convolution of the matrix-element weighted, orbitally resolved density of states.

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1. Introduction

In 1903, first Heusler alloys (HA) have been singled out as a special group of magnetic materials that exhibit ferromagnetism in compounds of non-magnetic elements [1]. Currently, the Mn-based half-Heusler alloys with the generic formula $XMnZ$ (with X being a $3d$ metal and Z belonging to the III or IV group) are well known magnetic systems that crystallizes in the Heusler $C1_b$ structure, which is closely related to the zincblende structure. Especially, the half-metallic ferromagnet NiMnSb [2] has been triggered a variety of experimental and theoretical investigations due to the search for materials to be used as spin-injectors. These materials are defined as magnetic materials with a band gap at the Fermi level for electrons of one spin direction. Band structure calculations for bulk NiMnSb show a gap of about 0.5 eV at $T=0$ for the

minority electrons, which means 100% spin polarization at the Fermi level E_F . In fully relativistic calculations a reduced but not vanishing gap and 99% spin polarization at E_F are predicted [3]. As in the case of the group III-V semiconductors, the crystal structure is the reason for the band gap. It is, therefore, called a covalent band gap [4]. As a consequence, the crystal structure and the site occupation within the given structure are important for the appearance of the gap. Atomic disorder, especially interchange of atoms between the Ni and Mn sub-lattices, results in a strong reduction of the spin polarization at E_F [5]. However, this interchange costs approximately as much energy as the evaporation of the metallic constituents [4]. Therefore, half-metallic behavior is an idealization distorted by structural inhomogeneities [6, 7, 8] and through the decrease of the spin polarization of spin carriers and vanishing of the semiconducting band gap for minority spin electrons in real crystals and interfaces caused by finite temperature effects.

A variety of experimental results for NiMnSb is available in the literature. While bulk measurements support the half-metallic behavior (see, e.g., [9, 10]), surface-sensitive techniques have failed so far to detect the energy gap for minority electrons or the 100% spin polarization at the Fermi level E_F . Most of the studies were performed on polycrystals or thin films, single and polycrystalline, prepared under various growth conditions on a variety of substrates. Spin-integrated photoemission (PE) spectra obtained with a photon energy of 45 eV showed clear signatures of the Ni and Mn $3d$ contributions [11]. Angle-integrated PE with variable photon energies identified Ni and Mn $3d$ emission from the valence bands emphasized the need for further careful investigations both experimentally and theoretically [12]. A spin-polarized PE study found values of the spin polarization up to 50% near photothreshold [13]. The authors concluded that, if an energy gap for minority electrons should exist, it is smaller than 0.5 eV. A further spin-resolved PE work, yet with photon energies between 38 and 76 eV, reported spin polarization values of at most 40% close to the Fermi level [14]. A reduced surface magnetization at remanence and/or a surface phase different from the bulk were proposed as possible explanations for the unexpected low polarization values. Furthermore, an angle-resolved photoemission study of the electronic structure single-crystalline NiMnSb sample showed that the binding energies of the photoemission intensities are sensitive to the particular surface condition and/or preparation [15]. Additionally, a possible surface state has been found in these \mathbf{k} -resolved measurements. In another study, a temperature-dependent cross-over from half-metallic to normal ferromagnetic behavior at 80 K was reported and discussed as a possible reason for the detected low polarization [16]. It was suggested that, at room temperature, the spin polarization at E_F may be considerably lowered due to a populated minority band, although the magnetization is not much reduced compared to the value at $T=0$. (With a Curie temperature of about 730 K, the magnetization at room temperature amounts to $\approx 92\%$ of the saturation value [17].) However, even point contact Andreev reflection measurements at 4.2 K at the free surface of NiMnSb gave a maximal value of only 44%, independent of different surface preparations and magnetic domain structures [18]. This result is in line with former spin-polarized PE data, which did not find a higher polarization value for 20 K than for room temperature [13]. As a complement to the reports above, a room-temperature study by angle and spin-resolved inverse photoemission reported close to 100% spin polarization at E_F and $\bar{\Gamma}$ under some conditions [19]. Last but not least from a spin-resolved Appearance Potential Spectroscopy (APS) study the measured spin asymmetry from the surface region was found to be significantly reduced compared to the theoretical prediction

[20].

In this contribution, we present spin-integrated and spin-resolved APS spectra from NiMnSb(001) and discuss by comparison with experimental data the degree of spin polarization as a function of chemical disorder. The paper is organized as follows. Section 2 is devoted to some experimental and computational details. In section 3 we discuss the theoretical results and compare with corresponding experimental data. A summary is given in section 4.

2. Experimental and computational details

2.1. Spectroscopical scheme

In this section the relevant details of the experimental investigations are given. A more delayed report can be found in Ref. [20].

APS is a surface sensitive tool to study the unoccupied density of states (DOS) with elemental resolution [21]. For spin-resolved APS, the sample is bombarded with a spin-polarized electron beam of variable energy while the total yield of emitted x-rays or electrons is monitored [22, 23]. At energies high enough to excite a core electron into empty states above the Fermi level, the yield of emitted particles increases due to recombination of the created core hole via x-ray or Auger electron emission. In our case, we detect the emitted x-rays [24]. Potential modulation together with lock-in techniques are used to separate the small signal from the dominating background. Since both the exciting and the excited electron are scattered into empty states, the rate of possible excitations and, thereby, of detected recombinations depends on the DOS above E_F . The spin-polarized electron beam used for excitation is emitted from a GaAs photocathode irradiated with circularly polarized 830 nm laser light. This arrangement provides about 30% spin polarization of the emitted electrons [25]. The spectra shown have been renormalized to 100% hypothetical beam polarization. The APS signal depends on the spin of the exciting electron in the case of ferromagnets because of the spin-dependent unoccupied DOS. The elemental resolution comes from the fact that core levels are involved whose energies are characteristic of the various elements.

2.2. Computational scheme

Hence, the calculational procedure concerning APS is found in detail in [20, 26] we restrict ourselves on a short description of some computational details. The fully relativistic DOS calculations have been performed within the SPRKKR computer program [27] running in the CPA-mode [28]. The chemical disorder introduced in the spectroscopical analysis consists of an interchange between Mn atoms on Ni sites and vice versa with concentration values x of 0%, 5%, 10% and 15%. This means we have calculated $(\text{Ni}_{1-x}\text{Mn}_x)(\text{Mn}_{1-x}\text{Ni}_x)\text{Sb}$ in the $L2_1$ crystal structure using the experimental lattice constant 5.91 Å. In Figs. 2 and 3 we use the compact notation $\text{Ni}_{1-x}\text{Mn}_x\text{Sb}$. Figure 1 shows the spin-resolved total DOS for NiMnSb. Clearly visible is the closing of the spin-dependent gap at the Fermi energy caused by the chemical disorder. Even at 5% interchange of Mn and Ni atoms the gap completely vanishes because the spectral weight is shifted towards the Fermi level. A significant enhancement of the spectral weight around the Fermi level is also observable in the majority DOS and therefore affect the amount of spin polarization that is measured

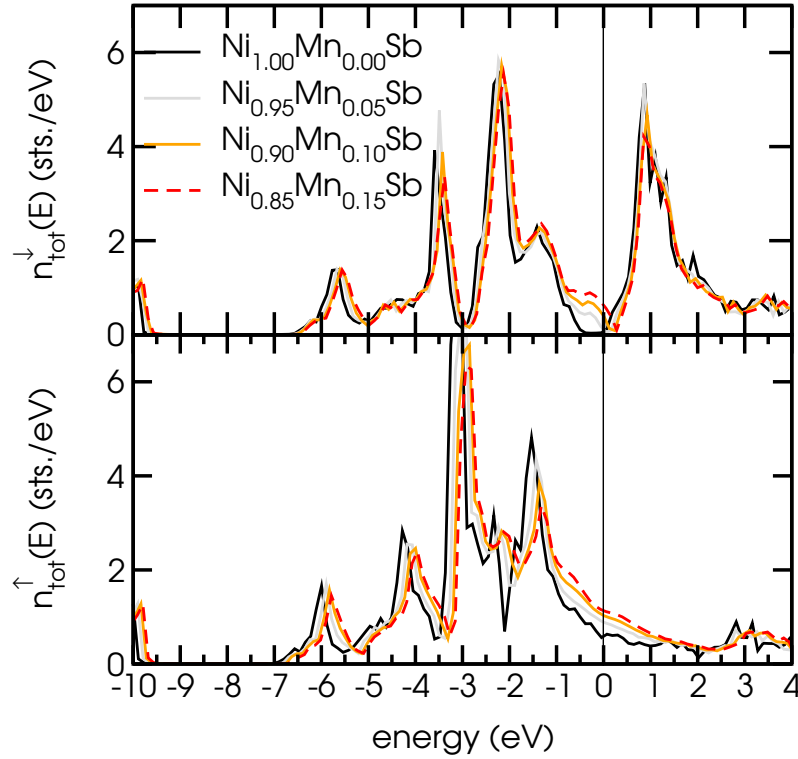


Figure 1. Spin-resolved total DOS for NiMnSb as a function of chemical disorder. The gap in the minority spin channel closes with increasing disorder induced by interchange of Mn and Ni atoms

in an APS experiment. The corresponding partial densities of states together with the spin-dependent potentials serve as input quantities for the spectroscopical calculations. In our case we probed the local DOS (LDOS) at the Mn atom in NiMnSb. The surface sensitivity is a result of the short mean free path of the electrons in the solid for energies that correspond to the Mn_{2p} excitation ($\approx 640\text{-}650$ eV). The elemental resolution results from the fact that a core level with an element-specific binding energy is involved. Due to the excitation with spin-polarized electrons the APS method becomes a magnetically sensitive technique. The calculated spin-dependent APS-intensities result from the weighted self-convolution of the corresponding LDOS. The weighting factor itself is given by the spin-dependent effective cross section consisting of an appropriate combination of relativistic Coulomb matrix elements. For a quantitative comparison between APS measurements and theoretical spectra one has to take into account various lifetime effects and the experimental broadening. Electron lifetime effects have been included in our analysis in a phenomenological way introducing a parametrized complex inner potential with an imaginary part of $V_{0i} = 30$ eV. The core hole lifetime is set to zero. Lifetime effects in the valence-band states are accounted via a Lorentzian with an energy-dependent width. For the explicit parametrization of the Lorentzian the reader is referred again to [20]. Strong correlations manifest themselves in form of the simple scaling factor $\lambda = 0.7(E - E_F)$. Furthermore, due to experimental conditions the first derivative of the APS signal has to be calculated

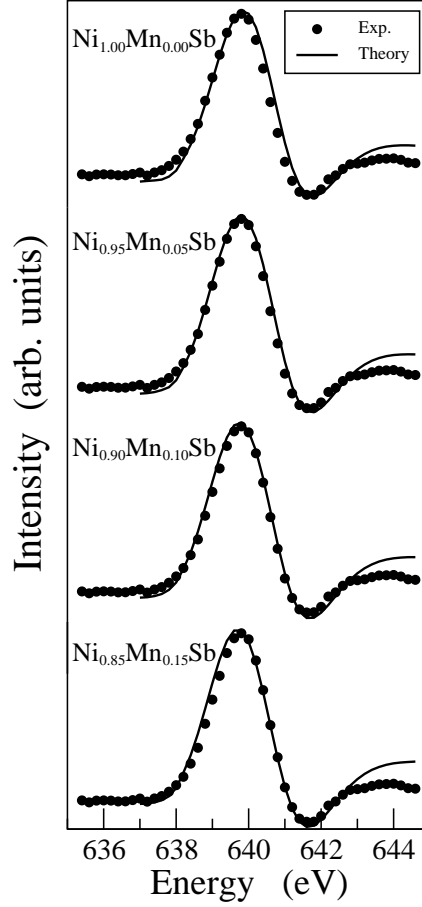


Figure 2. Spin-integrated AP spectra for NiMnSb(001) at the Mn $2p_{3/2}$ threshold as a function of chemical disorder. Experimental data are given by filled circles

and the apparatus broadening is considered by convoluting the calculated spectra by a Gaussian of $\text{FWHM} = 1.4$ eV.

3. Results and Discussion

Figure 2 presents calculated spin-integrated AP spectra for NiMnSb(001) in comparison with APS data. The spectra are normalized to equal maximum intensity. The theoretical spectra have been calculated with respect to the Fermi level. To be comparable with the experiment the calculated spectra were shifted along the energy axis until the peak maxima of the measured and calculated spectra coincidence. As it can be seen good agreement between experiment and theory is achieved. The almost quantitative agreement suggests that the DOS as calculated resembles the Mn local DOS in NiMnSb quite well in the spin-integrated case. The spectra show a pronounced structure at 639.7 eV from the Mn $2p_{3/2}$ threshold. These feature originate from the self-convoluted local density of unoccupied $3d$ states. The spectral feature at the high-

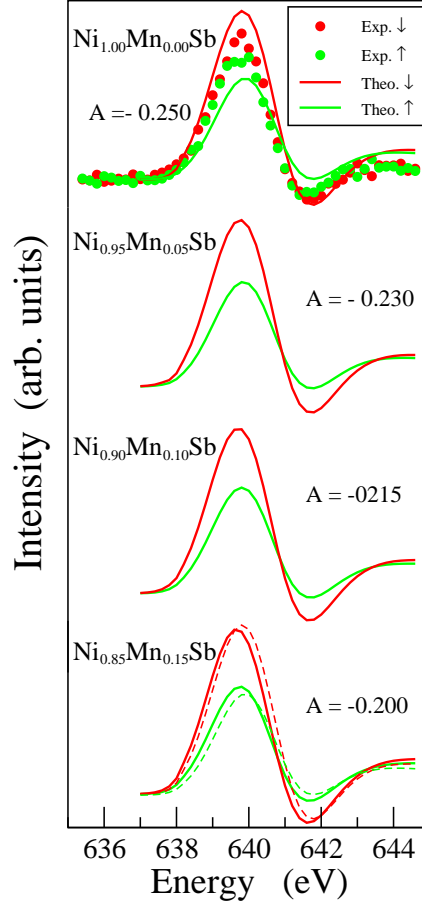


Figure 3. Spin-resolved AP spectra for NiMnSb(001) at the Mn $2p_{3/2}$ threshold as a function of chemical disorder. Experimental data are given by filled circles

energy side of the main line corresponds to the maximum of the sp -like DOS, whose appearance and energetic position is sensitive to the short-range crystallographic order around the atom where the local excitation occurs. As expected, the effect of chemical disorder is nearly negligible concerning the spin-integrated DOS. Only slight deviations in the APS line shapes between the spectra calculated for the ordered and for the disordered structures are observable.

By adding spin resolution (see spectra in Fig. 3), we are able to obtain information about the spin-dependent DOS. The experimental data for majority (\uparrow) and minority (\downarrow) spins are presented by black and grey open circles, respectively. First of all, the APS lines show a clear spin asymmetry, A , between the spin-dependent intensities I_{\uparrow} and I_{\downarrow} [$A = (I_{\uparrow} - I_{\downarrow}) / (I_{\uparrow} + I_{\downarrow})$]. The experimental spin-resolved spectra of Fig. 3 represent an average from many different surface regions. By taking into account the reduced remanent magnetization [20], we end up with an estimated spin asymmetry of $A = -0.115 \pm 0.012$ for a NiMnSb sample with saturated magnetization. The negative asymmetry reflects the high density of unoccupied minority states in NiMnSb, i.e. the unoccupied minority Mn $3d$ states. The theoretical spectra calculated for the

ordered structure, however, predict a higher negative spin asymmetry in the main APS peak of $A = -0.250$. This discrepancy between experiment and theory by a factor of two and more is in line with the findings of earlier spin-resolved electron spectroscopic experiments. Introducing chemical disorder the calculated value for the spin asymmetry decreases. This has to be expected because of the pronounced increase of spectral weight in the majority spin DOS around the Fermi energy that overcompensates the shift of spectral weight in the minority spin DOS. The concentration dependence of the spin asymmetry is demonstrated by the series of spin-dependent APS data shown in Fig. 3. The spin asymmetry in the main peak is calculated to $A = -0.230$ for 5% interchange of Ni and Mn atoms and decreases from $A = -0.215$ for 10% disorder to $A = -0.200$ for 15% interchange of Ni and Mn atoms. As a guide for the eye we compare at the bottom of Fig. 3 directly the spectra which belong to zero and 15% disorder to clarify the decrease in the spin asymmetry. Therefore, our analysis supports the result found by Orgassa et al. that chemical disorder significantly lowers the spin polarization at E_F . On the other hand, introducing the effect of chemical disorder to our APS calculations, we end up with an improved agreement between experiment and theory but the predicted spin asymmetry is still too high by nearly a factor of two. Our analysis indicates that other mechanisms besides chemical disorder must be taken into account for a quantitative explanation of the strongly reduced spin polarization in NiMnSb(001).

4. Summary

We have presented spin-integrated and spin-resolved APS data for the unoccupied electronic states of NiMnSb as a function of chemical disorder. The calculated series of spin-resolved and concentration dependent APS spectra demonstrates that chemical disorder influences the spin asymmetry of the unoccupied states of NiMnSb. Concerning the spin polarization at the Fermi level, one must note that APS is not particularly sensitive in that region. The nature of the APS signal doesn't allow one to resolve small energy gaps of the order of 0.5 eV giving rise to a positive spin asymmetry at E_F . The APS signal is rather dominated by the minority d states above E_F leading to a negative spin asymmetry. On the other hand the significantly reduced spin polarization observed in the experiment clearly indicates an uncomplete spin polarization with a value well below 100%. Therefore, the expected 100% spin polarization at the Fermi level is not verified, as in a number of spin-polarized electron spectroscopic experiments before. Furthermore, one has to take into account other mechanisms than chemical disorder to be able to explain quantitatively the unexpected low value for the measured spin asymmetry. Therefore, we conclude that the following issues must be examined in future studies on well-defined samples. First the magnetization within the surface layers compared with the bulk should be investigated in more detail. Also surface phases with respect to composition and/or crystallographic order different from the bulk could be important and the position and width of the band gap should be analyzed in more detail in the calculations. A first study on NiMnSb(110) showed the formation of microstructures upon preparation, which has consequences for the magnetic properties of the surface [29]. Even with a stoichiometric surface, the number of nearest neighbors is changed at the surface and surface/interface states may form and influence the gap [30, 31]. In the case that the free surface will not provide 100% spin polarization, there is still hope that specific interfaces may open the way for 100% spin-polarized charge-injection [32] in

spintronic devices. Other materials with half-metallic behavior must be considered as well in order to design functional materials for future applications [33].

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